4-1-1995

The Effect of environment on latent image formation and stability

Sean O'Toole

The Effect of Environment on Latent Image Formation and Stability

Sean W. P. O'Toole

B. S. State University College at Brockport, Brockport, New York

(1975)

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the Center for Imaging Science, Rochester Institute of Technology.

April, 1995

Signature of the Author: _____

Accepted by: Dana G. Marsh April 12, 1995

Coordinator, M. S. Degree Program

Center for Imaging Science

Rochester Institute of Technology

Rochester, New York

CERTIFICATE OF APPROVAL

M. S. DEGREE THESIS

The M. S. degree thesis of Sean W. P. O'Toole

has been examined and approved by the thesis committee as

satisfactory for the thesis requirement for the Master of Science degree.

Prof. Richard K. Hailstone, Thesis Advisor

Dr. Judith M. Harbison

Dr. Robert A. Curtis

4/7/95

Date

Thesis Release Permission Form

Rochester Institute of Technology

Center for Imaging Science

Title of Thesis: **The Effect of Environment on Latent Image Formation and Stability**

I, Sean William Padraic O'Toole, hereby grant permission to the Wallace Memorial Library of R. I. T. to reproduce this thesis in whole or in part. Any reproduction will not be for commercial use or profit.

Signature: _____

Date: 12 April, 1995

The Effect of Environment on Latent Image Formation and Stability.

Sean W. P. O'Toole

Submitted to the Center for Imaging Science in partial fulfillment of the requirements for the degree of Master of Science, Rochester Institute of Technology.

Abstract:

This thesis uses an unsensitized emulsion and two chemically sensitized emulsions to investigate the effect of oxygen and water vapor on latent-image formation and stability. At exposure times that cause little or no low-intensity reciprocity failure, vacuum treatment of an emulsion can result in photographic speeds significantly lower than those found in a humidified environment. This is presumably due to competition between intemal desensitization sites and surface electron traps for conduction-band electrons. Storage of a latent image in a humidified air environment will induce a speed loss in some emulsions. The unsensitized emulsion was most sensitive to environmental factors while the sulfur-plus-gold-sensitized emulsion was not. This is presumably due to the composition and size of the latent image. Maximum changes in photographic speed over time require the presence of both oxygen and water vapor. Oxygen alone may cause latent-image decay in some emulsions. Water vapor in a nitrogen environment did not affect latent-image stability. Extended development and gold latensification restored some of the speed loss observed with the unsensitized emulsion. The unrecovered speed loss is due to either latent-image centers being completely oxidized, or being too small to respond to chemical latensification.

Acknowledgments

The author would like to extend his appreciation and thanks to Professor Richard K. Hailstone, his thesis advisor. This study would not have been possible without his patience, knowledge, and guidance.

The author would like to extend his appreciation to Gary DiFrancisco for precipitating and sensitizing the emulsions used in this thesis, and for ensuring that there was always an ample supply of processing chemistry and other consumables.

The author would also like to extend his appreciation to Dr. Judith M. Harbison of the Eastman Kodak Company. Her guidance and encouragement have been a great asset and the author is very grateful for her time and patience.

A special thank you is due Dr. Robert A. Curtis of the Eastman Kodak Company. Dr. Curtis has been mentor, *advocatus diaboli*, a source of encouragement, and a friend. Without his support, this work would not have been possible.

Lastly, I would like to extend my appreciation to the many scientists and technical staff members of the Eastman Kodak Company who have critiqued this work.

Dedication.

Over the past five years, there has been one person waiting patiently on the "widow's walk;" waiting for her husband to come home. She has been steadfast in her support and encouragement. I look forward to becoming well acquainted with her again. Therefore, I dedicate this thesis to my wife and best friend, Laura Louise Viscome-O'Toole.

"Hi, Elizabeth, it's Daddy. Tell Mommy that I'm on my way home."

Table of Contents

List of Tables in Text

List of Tables in Appendix

List of Figures

I. Introduction

The effect of environment on photographic materials has been studied for over one hundred twenty years. Previous investigators have found that atmospheric components, such as water vapor and oxygen, can affect the photographic speed and developable density of a silver halide emulsion. Most investigators have used exposure times of tens to thousands of seconds to study the effect of environment on a multitude of emulsions. Extended exposure times are used to maximize the signal-to-noise ratio, but they can also cause a significant amount of low-intensity reciprocity failure (LIRF) in photographic materials.

Some work has been performed to examine the relationship between environment and latent-image stability over time. Difficulties associated with this type of study have limited the scope of these investigations. Examples of these difficulties include pre- and post-exposure conditioning of the test emulsions and the handling of materials in a reproducible manner.

The purpose of this study was to investigate how oxygen and water vapor can affect photographic materials using an exposure time that causes minimal LIRF. The effects of oxygen and water vapor were determined by observing latent-image stability and initial photographic speed in several environments. An unsensitized and two chemically sensitized emulsions were used to observe the effect of chemical sensitization on latent-image formation and stability.

A summary of several previous investigations concerning the effect of oxygen and water vapor on latent-image formation and stability is presented in the next section of this thesis. The experimental section will outline the methodology. Results will then be presented. Included are tables displaying the changes in photographic speed relative to a reference

point and graphs of several phenomena. The importance of chemical sensitization relative to latent-image formation and stability will be discussed. Also, the photographic speed advantage that vacuum-treated materials are known to have over materials conditioned to room air will be shown to be sensitive to exposure time, length of pre-exposure conditioning, and chemical sensitization. Tables of the measured photographic data are presented in the appendix.

II. Previous Investigations

The following paragraphs outline several selected investigations relevant to this thesis. *The Theory of the Photographic Process*, edited by T. H. James, is an additional reference for many of the topics discussed in this section.[1]

In 1872, Lt. Col. Wortley[2] wrote to the *British Journal of Photography* concerning photographic sensitivity. In his letter, Wortley states that he treated his photographic plates to "a couple of hours of strong heat" and that this increased the speed of his emulsion. He goes on to state that this increase in speed was lost after three days.

The editors of the *Journal* studied the photographic plates Wortley sent with his letter and noted that the colonel was reporting from Naples, Italy. The editors[3] suggested that he was observing the effect of relative humidity on his photographic plates. Naples, being a Mediterranean coastal city, has an elevated relative humidity due to the warm, sea air. Wortley's heat treatment removed atmospheric water from the plates and increased the photographic speed of the emulsion. After three days of reconditioning to the ambient climate of Naples, his plates had returned to their "ordinary degree of humidity" and the speed gain was lost.

Phrases such as the "ordinary degree of humidity" are not a quantitative measure or description of an emulsion's moisture content. A brief discussion concerning the relationship between moisture content and atmospheric relative humidity (% RH) is worthwhile.

Colton and Wiegand[4] reported that the moisture content response to a particular relative humidity is unique to that material. The more gelatin present, the higher the moisture content will be at any given relative humidity. At 0% RH, the moisture content of a gelatin layer is approximately zero. It should be noted that water molecules may still be present, but hydrogen bonded to the gelatin. This hydrogen bonding may inhibit the removal of water. A roughly linear relationship exists between moisture content and relative humidity from 20% to 60% RH. In this region, a large change in relative humidity is required to significantly change the moisture content of a film. Above 60% RH, moisture content rises in an almost exponential fashion.

An absolute moisture content value is meaningless outside of a particular gelatin-emulsion-support combination. Therefore, relative humidity is used to qualitatively describe the moisture content of an emulsion. Relative humidities between 20% and 60% are considered normal conditions. Increasing the relative humidity above 60% will generate a high moisture content. Photographic film layers in this moisture content range are soft, plastic, and longer in dimension. At relative humidities below 20%, the low moisture content will result in a hard, brittle film layer that is shorter in dimension.

Sheppard and Graham[5] investigated the effect of pH, pAg, and water (moisture) content on photographic speed. They found that speeds were at a maximum when the emulsion was conditioned to an atmosphere between 15% and 35% RH. This observation was valid

throughout the several pH and pAg regimes they studied. Peak sensitivity was found at about 20% RH.

Vanselow, Quirk, and Carroll[6] attempted to isolate the effects of water vapor and oxygen on latent-image formation. They used several spectrally sensitized motion picture emulsions and a control in their study. Their equipment was unique because it allowed for conditioning, exposure, and processing all to be performed within a test environment. They used humidified nitrogen and humidified oxygen environments to remove the interaction between oxygen and water.

These investigators found that a film treated in a humidified nitrogen environment was usually faster than a film treated in an oxygen environment at the same relative humidity. Their results also show that photographic materials treated in a 20% RH environment are usually faster than ones treated in an 80% RH environment for a given atmosphere. The undyed control material did not follow this trend.

The chemical sensitization of their control emulsion is not known. Given that Vanselow, et al., were studying motion picture emulsions, it is reasonable to assume that the control was chemically sensitized. Regardless of the exact chemical sensitization of the control, their results indicate that emulsions with different spectral sensitizations will have different responses to oxygen and water vapor.

James[7] discussed in detail the effects of pressure, moisture, and oxygen on latent-image formation. Pressure effects can be generated by using a dry gas or vacuum in emulsion studies. A dry environment will remove water from the gelatin matrix and cause it to contract. As the gelatin contracts, it can exert pressures up to 2000 kg/sq. cm and will desensitize a silver halide grain. It is thought that this desensitization is caused by a

deformation of the silver halide grain, although the mechanism is not understood.[8] If the pressure is kept below ~ 1000 kg/sq. cm, this desensitization is reversible. At pressures much above this level, desensitization is permanent.

Changing the moisture and oxygen content of an emulsion layer can affect latent-image formation and its stability. One possible mechanism[7] by which water and oxygen may affect the latent image is:

$$2\,Ag + {}^1/_2\,O_2 + H_2O \rightarrow 2\,Ag^+ + 2\,OH^- \qquad (1)$$

It is easy to assume from Reaction (1) that removing oxygen from an emulsion layer can increase the stability of the latent image. James notes, however, that not all emulsion layers are sensitive to oxygen. He reports that previous investigators are almost evenly split regarding the effect of oxygen on latent-image formation and its stability. It is important to note that these other investigators used a variety of emulsions that were chemically and/or spectrally sensitized. General statements about the effect of oxygen are difficult to extract from their data.

Water may have both a physical and a chemical role in latent-image formation and stability. One such chemical role is presented in Reaction (1) above. The physical role of water may be to swell the gelatin matrix. Swollen gelatin exerts almost no pressure on the surface of a silver halide grain, preventing any pressure-induced desensitization from occurring.[7] Swollen gelatin is also more permeable than dried gelatin. The more permeable the matrix is, the easier it is for oxygen and water vapor to reach the grain surface.

James[7] investigated the effect of exposure time on photographic speed at a particular time between exposing and processing. He exposed unsensitized emulsion samples to blue light

and used exposure times of 10^{-2} to 10^{4} s. Exposures were balanced so that approximately the same number of photons were striking the test emulsion regardless of exposure time. These exposures were performed in a variety of environments. For a 10^{4} s exposure, he found that vacuum-treated materials were 1.5 log E faster than those conditioned to 40% RH room air. At an exposure time of a few seconds to 10^{-2} s, there was very little difference between materials receiving a vacuum or room air treatment. This result would suggest low-intensity reciprocity failure as another factor for consideration in latent-image stability.

Armistead and Galimba[9] were interested in the latent-image stability of commercially available, high-resolution low-sensitivity photographic materials. These materials are useful for making holograms and for tracking nuclear particles. They chose three KODAK materials for study because they spanned a factor of 1000 in grain size and a factor of 3200 in photographic speed. The materials chosen were KODAK SO-343, fine grain positive, and commercial films. The samples were given a 10^{-4} s exposure through a 15-step density tablet to generate density-log relative exposure (D-log E) curves.

After two months of storage between exposing and processing under room air conditions, the SO-343 film lost over 70% of its density above base fog. The fine grain positive film lost 15% of its density above base fog. The commercial film lost less than 10% of its initial density in the upper scale regions of the D-log E curves.

Material handling techniques, such as exposing the SO-343 film samples in ambient air and then subjecting them to vacuum treatment, raise some concerns. Nevertheless, the vacuum treatment resulted in no loss of latent-image for SO-343 film samples. Treatment in dry oxygen produced a speed loss greater than that seen under room-air conditions. Armistead and Galimba concluded that oxygen is the major chemical agent for latent-image loss.

Platzer[10] investigated how the recombination of silver and bromine can affect latent-image stability. He used a weakly sulfur-sensitized emulsion as his test material. Samples were given a 10^{-3} s exposure through a step tablet. The test environments were: 25% RH air, 0% RH nitrogen, and ~100% RH nitrogen.

His materials were conditioned through a unique process. The samples initially received treatment in a vacuum to remove air and water vapor from the film samples. After this treatment, the test environment was then introduced into the vacuum chamber. The test materials then received two hours of conditioning in this new environment. Samples were then exposed and held in either the test environment or were subjected to a different environment immediately after exposure.

Platzer found that the only conditions that resulted in a stable latent-image were a dry nitrogen pre-exposure conditioning with dry or humidified nitrogen post-exposure conditioning, and humidified air pre-exposure conditioning followed by immediately submerging the samples in degassed water until processing. Using the same conditioning technique, he conditioned film samples to individual major atmospheric components to see if one of the gases induced a density loss. Since the dry gases did not induce a density loss, Platzer concluded that water is the main cause of latent-image loss.

He postulated a series of reactions between water and bromine (Br_2) to form hypo-bromate ($HBrO_3$). Hypo-bromate can then ionize to form hydrogen and a bromate ion. The bromate ion is stable in gelatin and can travel long distances through the matrix. Bromate also has the correct electrochemical potential to oxidize silver to silver bromide. Platzer suggested that bromate can be particularly effective at inducing a latent-image loss because it can remove up to six electrons at a latent-image site.

There are two potential problems with these experiments. One concem is the method used to condition samples to various environments. Previous investigators[7] have used a 16-hr pre-exposure treatment time, without evacuation, to condition materials to a particular environment. Two hours of post-vacuum conditioning in the test environment may not be sufficient time for the film to reach equilibrium with the test environment. There is also the possibility that the initial vacuum treatment may be inducing pressure desensitization and confounding his results.

A second problem with this study is the conclusion that water is the primary agent for latent-image decay. This is contradictory to his observation that samples stored in humidified nitrogen or submerged in degassed water until processing have a stable latent image. If water is the primary agent, then these treatments should have resulted in a significant loss of latent image.

Kuge, Fujiwara, and Hada[11] investigated a process indicating that there is a time delay in the formation of a latent image. A silver bromide cubic emulsion was precipitated and coated in a mono-grain layer format. This format is exceptionally thin so that the emulsion grains lay side-by-side on the support. The advantage of this format is that it is very convenient for counting developed latent-image sites on silver halide grains. The disadvantage is that there is little optical density available in this format. The only way to obtain useful data is to count latent-image sites on silver halide grains. Samples were conditioned in a vacuum environment for 16 h before exposure. After a $1.5*10^{-6}$ s exposure, samples were stored in the vacuum for up to 20 min before development.

Kuge, et al., found a 50% increase in the number of developable latent-image sites after 10 min of post-exposure vacuum treatment. This increase is seen at a mid-scale point on the

developable-center versus log relative-exposure curves. Introducing room air into the vacuum chamber stops all further increase in developable latent-image sites.

Kuge and Fujiwara[12] continued this work using various environments. The conditions they experimented with were dry air at 1 to 30 torr, dry air at normal pressure, ~100% RH nitrogen, 66% RH air, and vacuum as a reference check.

To varying degrees, the increase in the number of developable latent images with storage time was observed in all but the 66% RH room air environment. The investigators attribute this increase in developable latent images to mobile single silver atom species combining with subdevelopable latent images. Since an increase in the number of developable centers was observed in the saturated nitrogen environment, the investigators believe that oxygen is the primary factor for stopping this growth process. One way that oxygen could inhibit this growth process is to act as an electron trap and recombination center.

$$O_2 + e^- \rightarrow O_2^- \qquad (2)$$

$$O_2^- + \text{hole} \rightarrow O_2 + \text{recombination} \qquad (3)$$

III. Experimental

3.1 Emulsion. A 0.45 m AgBr octahedral emulsion was precipitated in gelatin. A sample of this emulsion was sulfur sensitized using 1.33 mg sodium thiosulfate/Ag mole. A second sample was sulfur-plus-gold sensitized using the same sodium thiosulfate level plus the addition of 2.00 mg potassium chloroaurate/Ag mole. These levels of chemical sensitizers are historically known to provide near optimum sensitization conditions for this emulsion.[14]

The unsensitized, sulfur-, and the sulfur-plus-gold-sensitized emulsions were coated on a clear acetate support at 100 mg Ag/sq. ft. with a hardened gelatin overcoat. The emulsion melts were adjusted to pH 5.5 and vAg 90 mV at 40° C before coating. Materials were cut into 12 inch by 35 mm film strips for ease of handling.

3.2 Sensitometer. Pre- and post-exposure conditioning of the film samples was done using an environmental sensitometer. This device is a modification of the stainless steel bell jar used by James, et al.[7,15] One modification is the incorporation of a 0 to 3.0 density, 15-step tablet into the exposure window. Eighteen film samples, in six groups of three, can be conditioned, exposed, and stored in a controlled environment until processing. Figure 1 is a sketch of the environmental sensitometer.

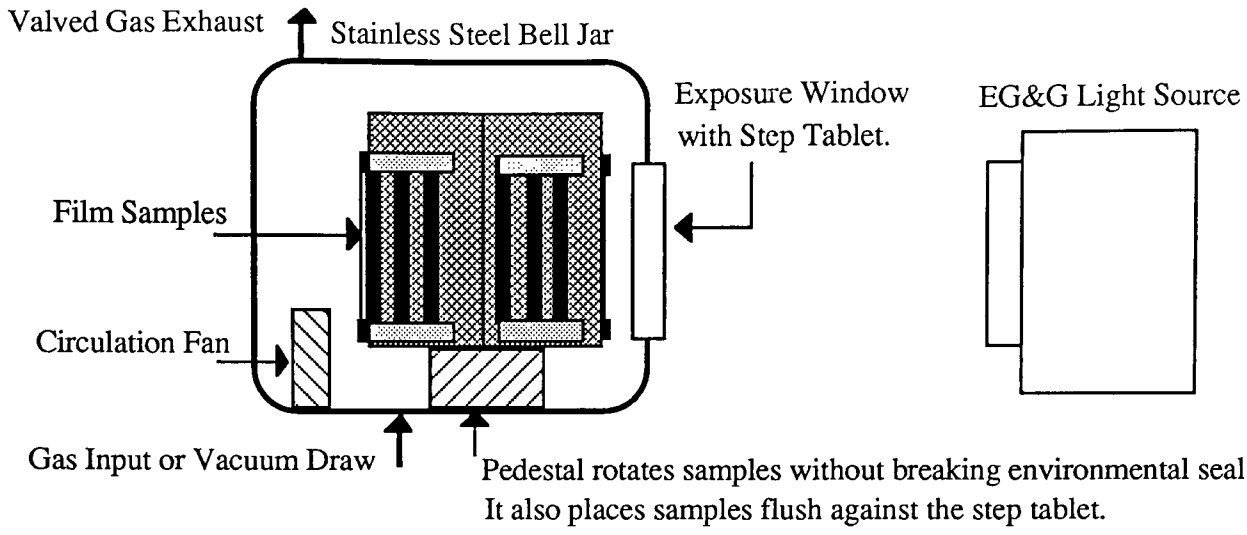

Figure 1. Environmental sensitometer.

Exposure times of 0.001 and 1 s were used to investigate the photographic response of the test emulsions in a regime where there is minimal or no reciprocity failure. The light source for the 0.001 s exposure was an EG&G Mark VII sensitometer. The EG&G sensitometer was placed so that its light source was perpendicular to the exposure window of the environmental sensitometer. A water-cooled quartz-halogen lamp was used for the 1 s exposure.

3.3 Environments. Seven different environments were chosen for study at the 0.001 s exposure time. They were 0% RH vacuum, air, and nitrogen; 20% RH air and nitrogen; and 80% RH air and nitrogen. Environments were restricted to 0% RH vacuum, air, and nitrogen; 20% RH air and nitrogen for experiments using a 1 s exposure time.

Materials were conditioned in a test environment for 72 h before the start of an experiment. A vacuum of 0.05 torr was generated by a mechanical pump with a molecular sieve trap to minimize oil back streaming. Nitrogen was supplied using commercially available

compressed gas cylinders. Air flow was provided by the building air supply. A preliminary study was done to compare the building air supply to a compressed air cylinder. No differences in sensitometry were found.

Relative humidity was controlled by bubbling the test gas through distilled water, cooling it to the desired wet bulb temperature using a water/glycol bath, and then allowing the gas to equilibrate to room temperature before its introduction into the environmental sensitometer. Relative humidity was checked using a hand held temperature/relative humidity probe placed in the gas effluent of the sensitometer. Figure 2 is a schematic of the humidity control system.

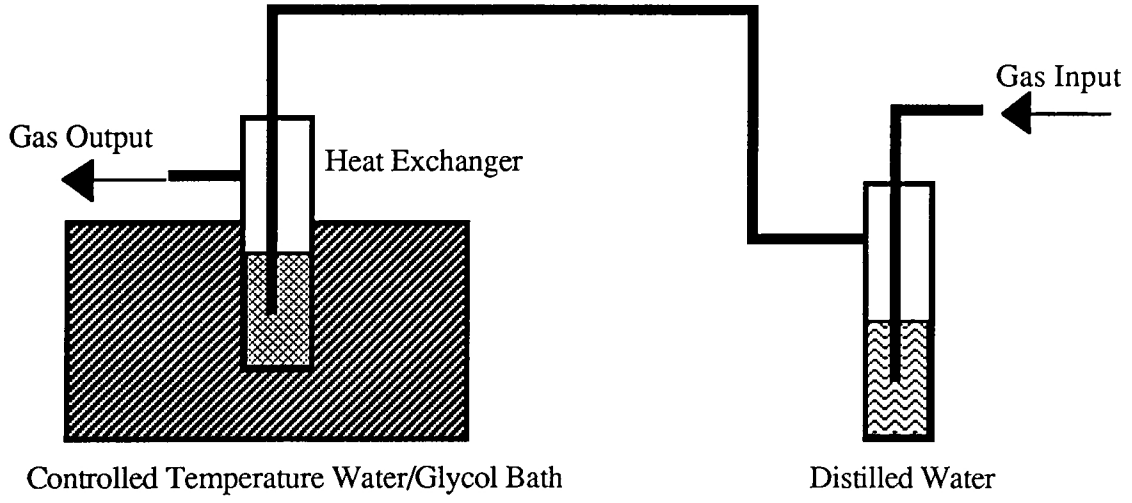

Figure 2. Gas humidification system.

3.4 Latent-Image Hold Times. Six different times between exposing and processing were chosen to study latent-image stability. They were 72, 48, 24, 4, 1, and 0.5 h of delay between exposing and processing. This sequence of times between exposing and processing is referred to as latent-image hold times or as the latent-image hold time profile. It was not possible to generate latent-image hold times shorter than 0.5 h due to the time

required to unseal the environmental sensitometer, remove the samples, and transport them to the processing laboratory.

An error of ± 2 s was allowed between the scheduled and actual exposure time during the last four hours of the latent-image hold time profile. An error of ± 15 min was allowed for the 24, 48, and 72 h exposure points.

3.5 Processing. Fresh, commercially available processing chemistry was used. KODAK D-19 Developer and KODAK Fixer were made within 72 h of scheduled processing. Film samples were developed for 6 min; immersed in a stop bath for 30 s; fixed for 5.5 min; and washed for 5 min. A 2 s burst of nitrogen was used every 7 s to agitate all the processing chemistry. A Wing-Lynch® temperature controller was used to maintain a 20° C processing temperature. After washing, the samples were placed in a forced-air drying oven for 30 min.

Six minutes of processing in KODAK D-19 Developer appears to develop five-atom and larger silver centers.[16,17] After 48 min of development, approximately 10% of the three-atom silver centers will initiate development, whereas larger metal clusters will have a 100% probability of initiating development. A latent image incorporating gold will be developable after 12 min of processing if there are at least three metal atoms in the cluster.

The optimum method of processing would be to process all 18 samples together in the same tank of developer. This procedure would also require a controlled-temperature processing tank that was several times larger than what was available. The best alternative was to process each sensitization type individually.

It was not physically possible to place three sets of samples into three separate processing tanks simultaneously. To compensate for this, the processing of the unsensitized and sulfur-plus-gold-sensitized emulsion samples were offset by ± 10 s around the desired processing time. The sulfur-sensitized materials were processed at 0.5 h after the last exposure. The unsensitized emulsion samples were placed in the developer 10 s before the sulfur-sensitized emulsion samples. The sulfur-plus-gold-sensitized materials were placed in processing chemistry 10 s after sulfur-sensitized materials. Error in processing time was estimated to be ± 1 s.

3.6 Gold Latensification. Gold latensification was performed on samples of the unsensitized emulsion. Materials were placed in a gold bath as described by James, Vanselow, and Quirk[18] for 10 min and then submerged for 5 minutes in a 1 g potassium bromide/L solution. Immediately following the potassium bromide bath, materials were processed using the procedure described in section 3.5.

3.7 Sensitometry. Film densities were measured using an X-rite® densitometer. These densities were then transferred to a computer that calculated photographic speed data. The point used for comparison in this thesis is photographic speed at base fog plus 0.50 density units (speed at D-min + 0.50). This point is approximately mid-scale on the density-log relative exposure (D-log E) curves for all the materials examined.

3.8 Data Presentation. Tables and graphs of the measured data are presented throughout this report. All data are presented in units of log relative exposure (log E). Given the same density value, a material with a large log E value is photographically slower than a material with a small log E value. This result is due to the first material requiring more light to achieve the desired density than the second material.

Tables and graphs of speed change are used to summarize the data. Change in speed over time uses the 0.5 h datum as the reference point for a given environment. The remaining five points of the latent-image hold time profile are compared to this point. The relative effect of environment on initial photographic speed will use the vacuum-treated materials as the reference point. Speed losses will result in negative values and speed gains will have a positive value. The reference point for these tables and graphs will have a value of zero.

Available data[19] suggests that a two standard deviation value of 0.04 log E is a reasonable estimate of the uncertainty in the measured speed. Thus, statistically meaningful differences are found only when data points are separated by at least 0.06 log E.

IV. Results

4.1. Photographic Response at 0.5 h Between Exposing and Processing.

Tables I and II present the change in speed data obtained for both exposure times and all three sensitizations. In general, there was no significant difference in speed between samples treated in humidified air and humidified nitrogen. Unsensitized emulsion samples treated in 20% RH nitrogen were 0.10 log E faster than those treated in 80% RH air. This difference was observed at an exposure time of 0.001 s.

The vacuum-treated materials were slower than materials treated in a humidified environment for both exposure times. Unsensitized emulsion samples receiving a 1 s exposure had only half the speed difference observed at a 0.001 s exposure. The unsensitized emulsion was the only material that was sensitive to exposure time in this regard. This sensitivity may be due to the onset of low-intensity reciprocity failure when using a 1 s exposure with this emulsion.

Sensitization type did affect the speed difference between the vacuum and the humidified environment treatments. The unsensitized emulsion had a difference of 0.29 to 0.39 log E between these treatments at a 0.001 s exposure. This speed difference was reduced to a range of 0.15 to 0.20 log E at the 1 s exposure. The sulfur-plus-gold-sensitized emulsion had a speed difference of 0.13 to 0.19 log E. The sulfur-sensitized emulsion had the smallest difference in speed between vacuum and humidified environments with values of 0.05 to 0.10 log E.

The measured speed values at 0.5 h of latent-image hold for all three sensitizations are presented in Tables IX and X of the appendix.

able I. Change in Speed for a 0.001 s Exposure and at 0.5 h of Latent-nage Hold.

	Delta Speed (log E) Relative to Vacuum.		
Environment	Unsensitized	Sulfur Sensitized	Sulfur-Plus-Gold Sensitized
Vacuum	0	0	0
0% RH N_2	0.10	-0.07	-0.09
0% RH Air	0.13	0.02	-0.07
20% RH N_2	0.39	0.10	0.17
20% RH Air	0.34	0.09	0.14
80% RH N_2	0.35	0.07	0.17
80% RH Air	0.29	0.05	0.13

able II. Change in Speed for a 1 s Exposure and at 0.5 h of Latent-Image [old.

	Delta Speed (log E) Relative to Vacuum.		
Environment	Unsensitized	Sulfur Sensitized	Sulfur-Plus-Gold Sensitized
Vacuum	0	0	0
0% RH N_2	0.12	0.07	0.16
0% RH Air	0.15	0.06	0.17
20% RH N_2	0.20	0.08	0.19
20% RH Air	0.15	0.06	0.17

4.2. Changes in Photographic Speed Over 72 h of Latent-Image Hold Time.

The unsensitized emulsion had the greatest loss of latent image over the 72 h test period. Tables III and IV indicate that a speed loss of 0.18 log E was observed in samples treated in a 20% RH air environment at both exposure times. The speed loss at 80% RH was not statistically different from the 20% RH air treatment at the 0.001 s exposure time. A speed loss was observed in 0% RH air at a 1 s exposure time. The speed loss observed at the 0.001 s exposure in 0% RH air was not statistically significant. Treatment of materials in the vacuum and nitrogen environments resulted in a stable latent image. Changes in speed for the unsensitized emulsion are shown in Figures 3 and 4.

The change in speed data for the chemically sensitized emulsions are presented in Tables V through VIII. With two exceptions, chemical sensitization resulted in a stable latent image for all environments studied. The first exception is for the sulfur-sensitized emulsion samples treated in humidified air. At a 0.001 s exposure time, a speed loss of 0.06 log E was observed over the first 24 h of latent-image hold (Table V). There was no continued fading of the latent image after the 24 h point.

The second exception is a speed gain between the 0.5 h and the 1 h latent-image hold times for the sulfur-plus-gold-sensitized emulsion. This gain was seen at the 0.001 s exposure (Table VII), but not at the 1 s exposure time (Table VIII). There are doubts whether this speed gain is real.

The measured speeds at the latent-image hold times are presented in Tables XI through XVI of the appendix.

Table III. Changes in Speed for the Unsensitized Emulsion at a 0.001 s Exposure.

	Delta Speed (log E) Relative to the 0.5 h Point.						
Hold Time	Vacuum	0% RH Air	20% RH Air	80% RH Air	0% RH N_2	20% RH N_2	80% RH N_2
0.5 h	0	0	0	0	0	0	0
1 h	0.02	0.03	-0.01	-0.02	0	0	0.01
4 h	0.02	0	-0.03	-0.03	0.01	0.03	0.03
24 h	0.04	-0.01	-0.12	-0.10	0.03	0.03	0.02
48 h	0.04	-0.04	-0.14	-0.12	0.03	0.03	0.03
72 h	0.05	-0.04	-0.18	-0.15	0.00	0.03	0.03

Table IV. Changes in Speed for the Unsensitized Emulsion at a 1 s Exposure.

	Delta Speed (log E) Relative to the 0.5 h Point.				
Hold Time	Vacuum	0% RH Air	20% RH Air	0% RH N_2	20% RH N_2
0.5 h	0	0	0	0	0
1 h	0.02	-0.02	0	0	0.03
4 h	0.02	-0.02	-0.05	0.02	0.04
24 h	0.02	-0.05	-0.12	0.02	0.05
48 h	0.05	-0.06	-0.15	0.03	0.06
72 h	0.03	-0.09	-0.18	0.03	0.05

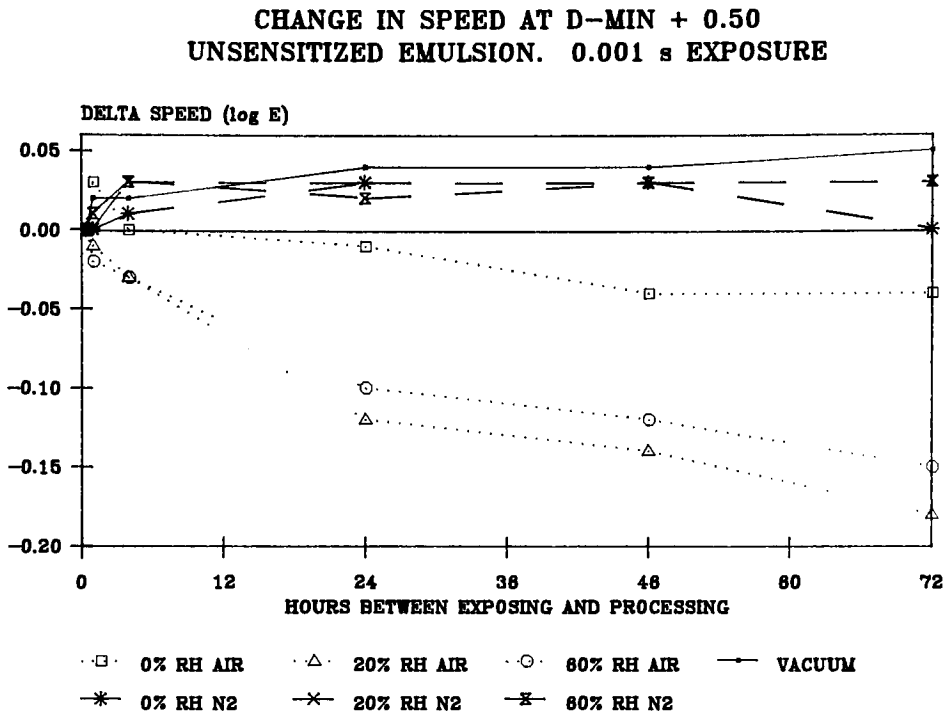

Figure 3. Relative Speed Loss Over Time for the Unsensitized Emulsion.

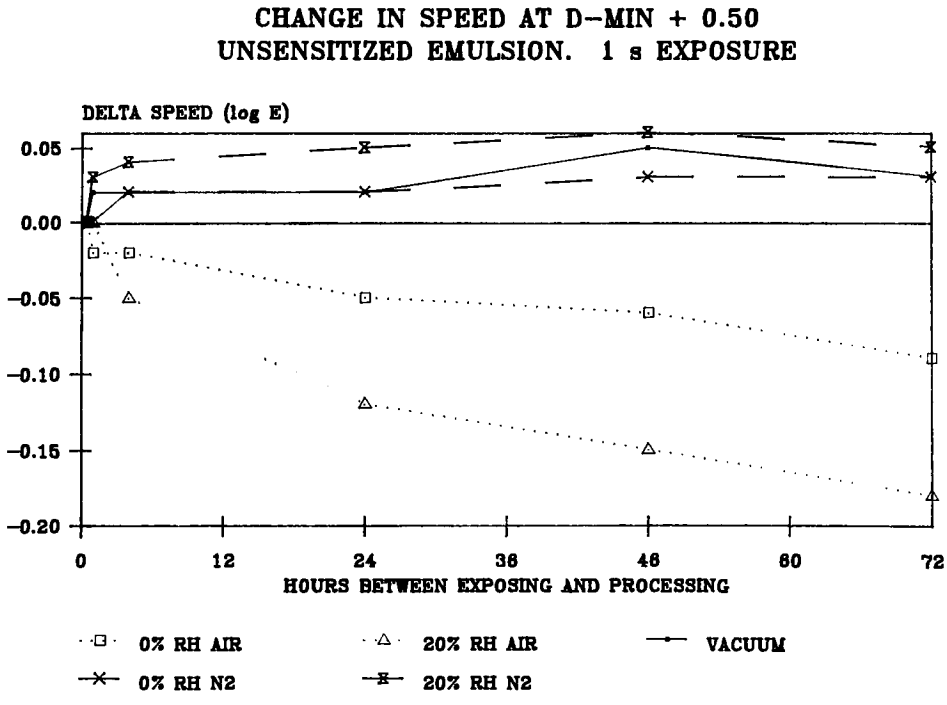

Figure 4. Relative Speed Loss Over Time for the Unsensitized Emulsion.

Table V. Changes in Speed for the Sulfur-Sensitized Emulsion at a 0.001 s Exposure.

	Delta Speed (log E) Relative to the 0.5 h Point.						
Hold Time	Vacuum	0% RH Air	20% RH Air	80% RH Air	0% RH N_2	20% RH N_2	80% RH N_2
0.5 h	0	0	0	0	0	0	0
1 h	0.01	0.01	-0.01	-0.01	0.01	0	0.01
4 h	0.02	-0.01	-0.03	-0.03	-0.01	0	0.01
24 h	0.02	0	-0.06	-0.06	0.01	-0.01	0
48 h	0.02	-0.01	-0.06	-0.03	0.02	-0.01	-0.02
72 h	0.03	0.00	-0.06	-0.05	0.03	-0.01	-0.01

Table VI. Changes in Speed for the Sulfur-Sensitized Emulsion at a 1 s Exposure.

	Delta Speed (log E) Relative to the 0.5 h Point.				
Hold Time	Vacuum	0% RH Air	20% RH Air	0% RH N_2	20% RH N_2
0.5 h	0	0	0	0	0
1 h	0	-0.03	-0.01	0	0
4 h	0	-0.03	-0.04	0.01	0
24 h	0	-0.02	-0.04	0.01	0
48 h	0.03	-0.02	-0.04	0.02	-0.01
72 h	0.02	-0.02	-0.03	0.04	0

Table VII. Changes in Speed for the Sulfur-Plus-Gold-Sensitized Emulsion at a 0.001 s Exposure.

	Delta Speed (log E) Relative to the 0.5 h Point.						
Hold Time	Vacuum	0% RH Air	20% RH Air	80% RH Air	0% RH N_2	20% RH N_2	80% RH N_2
0.5 h	0	0	0	0	0	0	0
1 h	0.01	0.07	0.01	0.01	0.01	0	0.02
4 h	0.01	0.07	0.01	0	0	0	0.01
24 h	0.02	0.05	-0.01	0	0	-0.01	0
48 h	0.03	0.08	-0.01	0.01	0.02	0.01	0.01
72 h	0.04	0.11	0	0.01	0.04	0	0.02

Table VIII. Changes in Speed for the Sulfur-Plus-Gold-Sensitized Emulsion at a 1 s Exposure.

	Delta Speed (log E) Relative to the 0.5 h Point.				
Hold Time	Vacuum	0% RH Air	20% RH Air	0% RH N_2	20% RH N_2
0.5 h	0	0	0	0	0
1 h	0.02	-0.01	0	0	0.01
4 h	0.01	0	-0.02	0.01	0.01
24 h	0.02	-0.01	-0.01	0.01	0.01
48 h	0.04	0.02	-0.01	0.03	0
72 h	0.04	0	0	0.03	0.02

4.3 Recovery of Subdevelopable Latent Images Through Changes in Minimum Developable Size. Experiments were performed to attempt recovery of the lost latent image in the unsensitized emulsion after 72 h of latent image hold time. The development time was extended to detect smaller latent-image sites. Three sets of six unsensitized emulsion samples were treated in a 20% RH air environment and a 72 h latent-image-hold-time profile was performed. Development times of 6, 24, and 48 min were used.

A development time of 6 min resulted in a speed loss of 0.20 log E over the 72 h hold time profile. Twenty-four minutes of development reduced the speed loss to 0.16 log E. After 48 min of development, the speed loss was reduced to 0.13 log E. As development time increased from 6 to 48 min, D-min increased from 0.04 to 0.17. (Appendix, Table XVII.) Extended development did recover some of the latent-image sites that had faded to below an Ag_5 center. This procedure also developed smaller fog sites that were not seen during a 6 min development in KODAK D-19 Developer. Figure 5 presents the change in speed over 72 h of latent-image hold for extended development.

Gold latensification was also used to attempt recovery of the sub-developable latent-image sites. Three sets of unsensitized emulsion samples were conditioned in a 20% RH air environment and a 72 h latent-image-hold-time profile was performed. One set was gold latensified using the procedure outlined in the section 3.6 of this thesis. A second set was submerged for 15 min in a solution containing 1 g potassium bromide/L. This pre-soaking treatment would account for any effect of gelatin swelling on development. The third set was kept in room conditions and was not pre-soaked before development. These materials were developed in KODAK D-19 Developer for 6 min. The speed loss data from this experiment are presented Figure 6.

Both the samples kept under room conditions and those presoaked in the bromide bath prior to development lost 0.18 log E over 72 hr. Samples receiving gold latensification lost 0.08 log E of speed during the same time period. This indicates that at least some of the lost speed is due to latent-image sites degrading to a sub-developable size. It is not known how much of the residual speed loss is due to latent-image sites not made developable through gold latensification or to latent-image sites being destroyed.

The measured data for the latensification experiments are presented in Tables XVII and XVIII in the appendix.

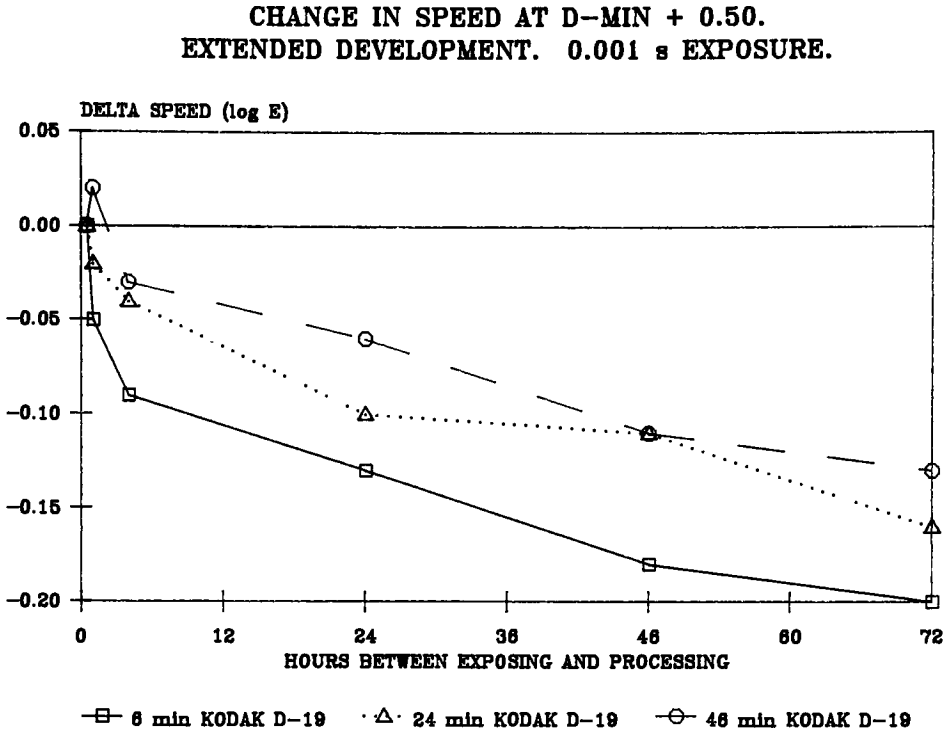

Figure 5. The Effect of Extended Development on Relative Speed Loss.

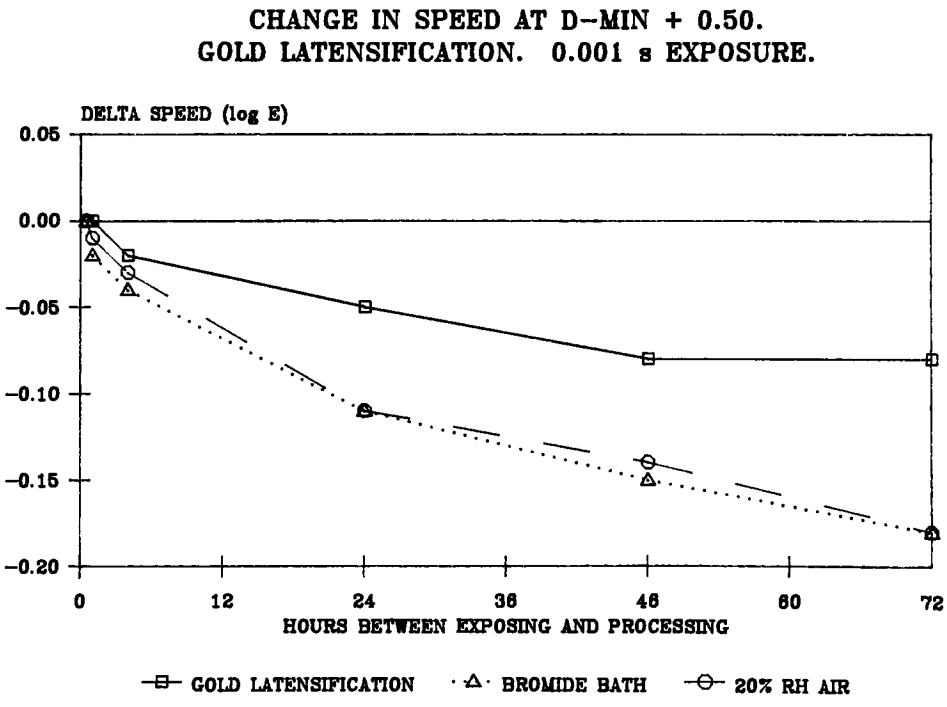

Figure 6. The Effect of Gold Latensification on Relative Speed Loss.

V. Discussion

5.1 Initial Photographic Speed at 0.5 h Between Exposing and Processing.

Materials treated in a vacuum environment were significantly slower than those treated in a humidified air environment regardless of exposure time. This is contrary to results published in many other studies. As mentioned above, James[7] found that exposure time has a significant effect when comparing photographic speeds in various environments. At long exposures of 10^4 s, there was significant difference in speed between materials conditioned in vacuum and room air. As exposure time was shortened to less than a second, this difference in speed became negligible in his investigation.

Long exposure times maximize the differences in photographic response induced by treatment in various environments. Low-intensity reciprocity failure occurs at these long exposure times. It is possible that, during a low-intensity exposure in humidified air, oxygen and water vapor are reacting with the latent image [Reaction (1)] and/or causing recombination of the conduction band electrons with holes [Reactions (2) and (3)]. The exposure times used in this thesis were positioned for minimal low-intensity reciprocity failure based on previously published reciprocity curves for similar emulsions.[20,21]

Pre-exposure conditioning technique may also affect the initial photographic speed. Traditionally, 16 h of pre-exposure conditioning has been used for environmental studies. Babcock, et al.,[13] found that conventional evacuation procedures may not remove all the oxygen from an emulsion layer. Oxygen and other residual materials can interfere with latent-image formation. In this thesis, the materials used to study the initial photographic speeds were conditioned for over 140 h before they were exposed. This extended conditioning was achieved by conditioning for 72 h before the start of the experiment and an additional 71.5 h between the start of the experiment and exposure at 0.5 h before

processing. One hundred forty hours of pre-exposure vacuum conditioning will likely remove the additional oxygen and water not removed during the traditional 16 h pre-exposure treatment.

The difference in initial photographic speed between the treatment in a vacuum and in a humidified environment is sensitization dependent. The unsensitized emulsion had the largest difference in speed between treatment in vacuum and humidified environments. The sulfur-plus-gold-sensitized emulsion had a smaller difference in speed between the two treatments. The sulfur-sensitized emulsion had the smallest difference in speed.

Electron traps are necessary for latent-image formation and the depth of the electron trap is sensitization dependent.[22,23] In an unsensitized emulsion, the surface electron traps are very shallow. Vacuum treatment may create internal defects that can successfully compete for trapping electrons and holes. These defect sites may lead to internal latent-image formation or internal recombination, resulting in fewer electrons being available to form a surface latent image. The latent images that do form will be smaller because some electrons are lost to these internal sites. Unsensitized emulsion samples conditioned to a humidified environment will not have vacuum-induced internal defect sites. This results in larger surface latent images and greater speed when compared with the vacuum treated unsensitized emulsion.

Exposure time may also affect the speed difference between the vacuum and humidified environment treatments for the unsensitized emulsion. In a high-intensity exposure, such as 0.001 s, a number of latent sub-images may form. These latent sub-images may compete with each other for available electrons. This competition will decrease the probability of forming a developable surface latent image. Latent-image dispersity is reduced as the exposure time increases. A longer exposure should result in fewer and

larger latent images as well as a greater probability of forming a developable surface latent image.

The hypothesis of latent-image dispersity is supported by the change in speed data presented in Tables I and II for the unsensitized emulsion at the 0.5 h latent-image hold point. The materials receiving a 0.001 s exposure had a speed difference of 0.39 log E between the vacuum and the humidified gas treatments. The materials receiving a 1 s exposure had a speed difference of 0.20 log E. A reduction of dispersity is the most logical explanation for the speed change decrease as exposure time increases.

Sulfur-sensitized emulsions also are subject to vacuum desensitization. However, the sulfur sensitization sites are able to successfully compete with any vacuum-induced internal desensitization. This will reduce the speed difference between exposures in a humidified environment and those in vacuum. Chemical sensitization will direct latent-image formation to the sensitization sites regardless of the environmental conditions. This effect is supported by the delta speed data in Tables I and II for the chemically sensitized emulsions.

The sulfur-plus-gold-sensitized materials have a greater speed difference between treatments in vacuum and the humidified environments than the sulfur-sensitized materials. The electron trap depth for a sulfur-plus-gold-sensitized emulsion is less than that of a sulfur-sensitized emulsion.[22,23] This difference in electron trap depths could indicate that an internal desensitization site is able to compete with greater success for electrons in a sulfur-plus-gold-sensitized emulsion. However, this would contradict previously published results indicating that latent-image formation in a sulfur-plus-gold-sensitized emulsion is less likely to be affected by an internal desensitization site than in a sulfur-sensitized emulsion.[24] Thus, we do not have an explanation for the greater desensitization

of the sulfur-plus-gold-sensitized emulsion than the sulfur-sensitized emulsion by vacuum treatment.

It would be possible to determine if internal latent images were being formed as a result of vacuum treatment by using a whole-grain developer instead of a surface developer. However, since latent-image stability was the primary focus of this thesis, these additional experiments were not done.

5.2 Latent-Image Stability Over 72 h of Latent-Image Hold Time.

Unsensitized emulsion samples treated in either a dry or humidified nitrogen environment do not show a speed loss over 72 h of latent-image hold time whereas treatment in an air environment does induce a speed loss.

The lack of a speed loss in the nitrogen environments indicates that nitrogen does not affect the stability of a latent image. The data also indicates that water vapor in an inert atmosphere will not degrade a latent image over 72 h of latent-image hold. These statements are also valid for the chemically sensitized emulsions studied in this thesis.

A speed loss was observed after treatment in dry air using a 1 s exposure. There is a trend, not statistically proven, indicating that treatment in a 0% RH air environment and using a 0.001 s exposure will also result in a speed loss over time. Extending the length of the latent-image hold time would verify whether a speed loss actually occurs as a result of treatment in 0% RH air.

Observing a speed loss after treatment in a dry air environment does not mean that oxygen is the only material available to react with a latent image. Flowing 0% RH air over the emulsion will dry the gelatin. However, not all the water will be removed.[4] Some water

will be trapped through hydrogen bonding with the gelatin or may be trapped on the grain surface. Water and oxygen can then degrade the latent image.

There are two possible reactions between oxygen and a latent image. Reaction (4) was presented earlier.

$$2\,Ag + {}^{1}/_{2}\,O_2 + H_2O \rightarrow 2\,OH^- + 2\,Ag^+ \qquad (4)$$

$$2\,Ag + {}^{1}/_{2}\,O_2 + 2\,H^+ \rightarrow H_2O + 2\,Ag^+ \qquad (5)$$

Reaction (5) is equivalent to Reaction (4), but appropriate for the acidic nature of the coating.

Water vapor may participate in the latent-image oxidation process as a reactant or as a transporter of protons. Evidence supporting the synergistic action of oxygen and water vapor is seen in the data for the unsensitized emulsion. A speed loss of 0.18 log E is observed after treatment in a 20% RH air environment for 72 hr. Treatment in a humidified air environment is much more conducive to speed loss than treatment in a 0% RH air environment. The presence of water is important to obtain maximum speed loss.

A third possible way that water can participate in the loss of latent image is by physically swelling the gelatin. Swelling the gelatin will increase the permeability of the emulsion layer. This will facilitate the flow of reactants to a latent-image site. It is quite possible that water may participate in all three ways simultaneously.

Colton and Wiegand[4] have indicated that water is still present in a dried emulsion layer. The question can be asked whether oxygen can degrade a latent image without the presence

of water. Lee and Ervin[25] found that it is possible for a negatively charged gas-phase silver cluster to react with oxygen.

$$Ag_n^- + O_2 \rightarrow Ag_nO_2^- \qquad (6)$$

This reaction may be a part of the reaction sequence shown in Reactions (4) and (5). The reaction rate is approximately ten times greater for an even-sized silver cluster than for an odd-sized silver cluster. Also, larger silver clusters react faster than smaller clusters.

Gas-phase gold clusters will react with oxygen in a fashion similar to that of gas-phase silver clusters. However, Lee and Ervin found that the oxidation rate for gold clusters is approximately ten times slower than the oxidation rate for silver clusters. This result would suggest that a gold-incorporated latent image would be less prone to oxidation than a silver-only latent image. The observations in this thesis for the sulfur-plus-gold-sensitized emulsions support this hypothesis.

The unsensitized emulsion was found to be more susceptible to latent-image fading in a humidified environment than the sulfur-sensitized emulsion. The observations made by Lee and Ervin may explain this result. An unsensitized emulsion often forms only one latent image when exposed to light. Sulfur sensitization directs latent-image formation to multiple sites on the surface of the silver halide grain. Assuming that the two materials have received exposures that will result in comparable densities and that the latent images in question are larger than the minimum developable size, the single latent image on the unsensitized emulsion grain will be larger than the multiple latent-images formed on the sulfur-sensitized emulsion grain.[26] Computer simulations of latent-image formation performed by Hailstone[27] support this statement. As a result, the larger latent image on the

unsensitized emulsion grain may have a greater probability of being oxidized than the smaller, multiple latent images on the sulfur-sensitized emulsion grain.

Investigations performed both by Tani and by Matsubara and Levy may also support the hypothesis that both size and composition of a latent image can affect the potential for oxidation. Tani[28] investigated the redox potential of the latent image by submerging variously sensitized emulsion samples in a redox buffer for up to 65 h and then processing the materials. He found that the unsensitized and the sulfur-sensitized emulsions both lost similar amounts of latent image due to treatment in the buffer. The sulfur-plus-gold-sensitized emulsion was stable. He attributes this stability to the high electronegative value of gold in the silver-gold centers.

Matsubara and Levy[29] performed similar experiments using a five minute treatment in the same type of redox buffer. They also found that the sulfur-plus-gold-sensitized emulsion was stable. However, Matsubara and Levy found that the unsensitized emulsion lost more latent image after treatment in the redox buffer than the sulfur-sensitized emulsion. They suggested that this observation may, in part, be due to silver sulfide being incorporated into the latent image of a sulfur-sensitized emulsion. The presence of silver sulfide in the latent image may change the oxidation characteristics of the latent image. This incorporation could explain why, at a 5-atom minimum developable size, a latent image in a sulfur-sensitized emulsion is more stable than a 5-atom latent image in an unsensitized emulsion.

Both investigations may be correct. Tani assumed that he had reached equilibrium after 65 h of treatment. Matsubara and Levy assumed that they were not in equilibrium. It is possible that the unsensitized emulsion has a higher initial rate of latent-image oxidation than the sulfur-sensitized emulsion. Once equilibrium is reached in the redox buffer, the unsensitized and sulfur-sensitized emulsions have similar loss of latent image. The difference in latent-

image loss rates between the unsensitized and the sulfur-sensitized emulsions in humidified air may support Matsubara and Levy's observations. Extending the latent-image hold time for the unsensitized and sulfur-sensitized emulsions in a humidified air environment could indicate whether an equilibrium would actually be obtained.

After 72 h of latent-image hold, gold latensification and extended development restored some, but not all the speed loss observed in the unsensitized emulsion. Extending development time can develop smaller latent-image centers. After 48 min of development in D-19, the speed loss was reduced to 0.13 log E. This partial recovery of the speed loss is probably due to latent-image sites smaller than an Ag_5 being developed.

Gold latensification reduced the speed loss from 0.18 log E to 0.08 log E after 72 h of latent-image hold. This result indicates a portion of the observed fading is due to latent images becoming too small for conventional development, but are still recoverable through gold latensification. Gold can combine with subdevelopable silver centers and form a developable silver-gold latent image.[18] It is not known what percentage of the remaining speed loss is due to silver centers that are not gold latensifiable, or to completely decayed latent-image centers.

Light latensification would be able to recover Ag_2 centers by using a very low intensity, long duration exposure.[30] This procedure takes advantage of low-intensity reciprocity failure in that only pre-existing latent-image sites will grow to developable size. Facilities were not available to perform this experiment.

VI. Conclusions

1. At exposure times that cause little or no low-intensity reciprocity failure, vacuum treatment of an unsensitized or chemically sensitized emulsion can result in speeds significantly slower than those found in a humidified environment. This result is contrary to results from investigators using a long duration exposure. The extended pre-conditioning technique used in this thesis may have removed additional oxygen and water vapor from the photographic materials. This procedure may have affected the speed difference between treatments in vacuum and humidified environments.

2. The unsensitized emulsion had a reduction in the speed difference between treatments in vacuum and humidified environments as the exposure time was increased. This reduction in the speed difference may be due to the onset of low-intensity reciprocity failure in the unsensitized emulsion. The sulfur- and sulfur-plus-gold-sensitized emulsions were not sensitive to this change in exposure time.

3. At 0.5 h between exposing and processing, the unsensitized emulsion had the largest difference in speed between treatment in vacuum and humidified environments. This speed difference is attributed to the creation of an internal desensitization site by the vacuum treatment. This internal desensitization site can compete effectively for conduction band electrons. The sulfur-sensitized emulsion had very little speed difference between the two treatments. This lack of a difference has been attributed to the depth of the electron trap at the sulfur-sensitization sites.

4. Storage of a latent image in a humidified air environment will induce a speed loss in some emulsions. The unsensitized emulsion lost significant speed over time whereas the

chemically sensitized emulsions were relatively stable. Chemical sensitization can affect the ability of a latent image to be oxidized.

5. Humidified nitrogen environments did not induce a speed loss over time. This result indicates that water alone does not affect the stability of a latent image in the unsensitized or chemically sensitized emulsions used in this thesis.

6. Oxygen appears to be the primary oxidizing agent for latent-image decay. The presence of atmospheric water vapor can accelerate this decay process. Both the size of the latent image and the sensitization of the silver halide grain can influence the stability of a latent image over time. Latent images incorporating gold were stable over the 72 h of latent-image hold time. The latent image in an unsensitized emulsion grain is much more readily oxidized.

7. Speed losses in the unsensitized emulsion treated in humidified air are a result of latent-image sites being made undevelopable. Gold latensification restored approximately 50% of the lost speed. The unrecoverable speed loss is due to latent-image centers being either completely oxidized or too small to respond to the chemical latensification procedures used.

VII. Future Work

1. Seventy-two hours of latent-image hold was used in this work. Extending this hold time would demonstrate whether the observations reported here continue.

2. Gold latensification and extended development did not restore all the speed loss observed in the unsensitized emulsion after 72 h of latent-image hold in a 20% RH air

environment. Light latensification would determine how much of the speed loss not chemically recoverable is due to the complete loss of latent image.

3. A surface developer was used in this thesis. The use of a whole-grain or an internal developer should recover any internal latent images formed by pressure desensitization Materials processed with a whole-grain developer should have a higher speed than samples processed with a surface developer.

4. Previous investigators have reported conflicting results regarding latent-image stability. Part of this conflict has been the introduction of spectral sensitizers. Adding spectral sensitizers to an emulsion with a known latent-image stability pattern could help resolve this conflict.

References

1 T. H. James, *The Theory of the Photographic Process*, 4th edition; Ch. 4, Sec. I. B-E; Ch. 5, Sec. I. A, C-E; Ch. 6. Sec. C.

2 Lt. Col. H. S. Wortley, "On Heat As a Means Of Increasing the Sensitiveness Of Dry Plates," *Brit. J. of Photo.* **19:**279 (1872)

3 "Action Of Heat On Dry Plates," *Brit. J. of Photo.* **19:**277 (1872)

4 E. K. Colton, E. J. Wiegand, "Moisture in Photographic Film and Its Measurement," *Photo. Sci. Eng.* **2:**3 (1958)

5 S. E. Sheppard, C. L. Graham, "Extragranular Factors In Photographic Sensitivity," *J. Franklin Inst.* **230:**619 (1940)

6 W. Vanselow, R. F. Quirk, B. H. Carroll, "The Effect Of Oxygen and Moisture Upon Desensitization In Photographic Emulsions," *Photo. Sci. & Technique* **18B:**11 (1952)

7 T. H. James, "Some Effects of Environment on Latent-Image Formation by Light," *Photo. Sci. Eng.* **14:**1 (1970)

8 T. H. James, *The Theory of the Photographic Process*, 4th edition; Ch. 5. Sec. II. D.

9 R. A. Armistead, F. B. Galimba, "Latent-image Fading of Three Commercially Available Fine Grained Emulsions," *Photo. Sci. Eng.* **17:**1 (1973)

10 S. J. W. Platzer, "Latent-image Fading in a Silver Bromide Emulsion," *Photo. Sci. Eng.* **22:5** (1978)

11 K. Kuge, S. Fujiwara, H. Hada, "Delayed Formation of Image Specks in Vacuum," *Photo. Sci. Eng.* **25:5** (1981)

12 K. Kuge, S. Fujiwara, "Effect of Environment on the Delayed Formation on Latent Image Specks," *Photo. Sci. Eng.* **27:5** (1983)

13 T. A. Babcock, B. P. Michrina, P. A. McHue, T. H. James, "Effects of Moisture on Photographic Sensitivity," *Photo. Sci. Eng.* **14:4** (1973)

14 Private communication G. DiFrancisco, Center for Imaging Science, Rochester Institute of Technology.

15 W. C. Lewis, T. H. James, "Effect of Evacuation on Low Intensity Reciprocity Failure and on Desensitization by Dyes," *Photo. Sci. Eng.* **12:2** (1969)

16 R. K. Hailstone, J. F. Hamilton, "Effect of a Distribution of Developable Sizes in Determination of the Minimum Size of the Latent-Image," *J. Image. Sci.* **32:6** (1987)

17 Private communication, Richard K. Hailstone, Center For Imaging Science, Rochester Institute of Technology.

18 T. H. James, W. Vanselow, R. F. Quirk, "Gold and Mercury Latensification and Hypersensitization for Direct and Physical Development," *J. Photo. Soc. Am.* **14:**349 (1948)

19 R. K. Hailstone, N. B. Liebert, M. Levy, R. T. McCleary, S. R. Girolmo, D. L. Jeanmarie, C. R. Boda, "Achieving High Quantum Sensitivities with Hydrogen Hypersensitization. 1. Measurement," *J. Image. Sci.* **32:**3 (1988)

20 R. K. Hailstone, N. B. Liebert, M. Levy, "Development Center Distribution in a AgBr Model Emulsion. 1. Sulfur-Plus-Gold-Sensitized Versions," *J. Image. Sci.* **32:** 150 (1988)

21 R. K. Hailstone, N. B. Liebert, M. Levy, "Development Center Distribution in a AgBr Model Emulsion. 2. Sulfur-Sensitized Versions," *J. Image. Sci.* **33:** (1988)

22 J. F. Hamilton, J. M. Harbison, D. L. Jeanmarie, "Energy Levels of Sulfur Sensitizer Centers," *J. Image. Sci.* **32:**17 (1988)

23 D. Zhang, R. K. Hailstone, "Electronic Properties of Sensitizer Centers," *J. Image. Sci. Tech.* **37:**1 (1993)

24 G. C. Farnell, L. R. Solman, "Further Comments on the Role of Gold in Sulfur Plus Gold Sensitization," *J. Photo. Sci.* **28:**185 (1980)

25 T. H. Lee, K. M. Ervin, "Reaction of Copper Group Cluster Anions with Oxygen and Carbon Monoxide," *J. Phys. Chem.* **98:**10023 (1994)

26 T. H. James, *The Theory of the Photographic Process*, 4th edition; Ch. 6. Sec. C.

27 Private communication of unpublished latent-image simulation data. Richard K. Hailstone, Center For Imaging Science, Rochester Institute of Technology.

28 T. Tani, "A Study of Properties of Clusters of Photographic Interest by Means of a Redox Buffer Solution," *Photo. Sci. Eng.* **27:**2 (1983)

29 T. Matsubara, M. Levy, "Redox Stability of the Latent-Image and Latent Subimage Centers of Unfinished, Reduction Sensitized, Sulfur Sensitized, and Sulfur-Plus-Gold Sensitized Octahedral Silver Bromide Emulsions," *J. Image. Sci.* **32:** (1988)

30 R. K. Hailstone, J. F. Hamilton, "On Detecting the Latent Subimage with Light Latensification," *J. Photo Sci.* **34:**154 (1986)

Appendix

Table IX. Measured Speed At 0.5 h Of Latent-Image Hold Time for All Sensitizations. 0.001 s Exposure Time.

	Speed at D-min + 0.50 (log E)		
Environment	Unsensitized	Sulfur Sensitized	Sulfur-Plus-Gold-Sensitized
Vacuum	3.73	2.82	2.66
0% RH N_2	3.63	2.89	2.75
0% RH Air	3.60	2.80	2.73
20% RH N_2	3.34	2.72	2.49
20% RH Air	3.39	2.73	2.52
80% RH N_2	3.38	2.75	2.49
80% RH Air	3.44	2.77	2.53

Table X. Measured Speed At 0.5 h Of Latent-Image Hold Time for All Sensitizations. 1 s Exposure Time.

	Speed at D-min + 0.50 (log E)		
Environment	Unsensitized	Sulfur Sensitized	Sulfur-Plus-Gold Sensitized
Vacuum	3.30	2.64	2.59
0% RH N_2	3.18	2.57	2.43
0% RH Air	3.15	2.58	2.42
20% RH N_2	3.10	2.56	2.40
20% RH Air	3.18	2.60	2.43

Table XI. Measured Speed Values For the Unsensitized Emulsion Over 72 h of Latent-Image Hold. 0.001 s Exposure Time.

	Speed at D-min + 0.50 (log E)						
Hold Time	Vacuum	0% RH Air	20% RH Air	80% RH Air	0% RH N_2	20% RH N_2	80% RH N_2
0.5 h	3.73	3.60	3.39	3.44	3.63	3.34	3.38
1 h	3.71	3.57	3.40	3.46	3.63	3.34	3.37
4 h	3.71	3.60	3.42	3.47	3.62	3.31	3.35
24 h	3.69	3.61	3.51	3.54	3.60	3.31	3.36
48 h	3.69	3.64	3.53	3.56	3.60	3.31	3.35
72 h	3.68	3.64	3.57	3.59	3.63	3.31	3.35

Table XII. Measured Speed Values For the Unsensitized Emulsion Over 72 h of Latent-Image Hold. 1 s Exposure Time.

	Speed at D-min + 0.50 (log E)				
Hold Time	Vacuum	0% RH Air	20% RH Air	0% RH N_2	20% RH N_2
0.5 h	3.30	3.15	3.18	3.18	3.10
1 h	3.28	3.17	3.18	3.18	3.07
4 h	3.28	3.17	3.23	3.16	3.06
24 h	3.28	3.20	3.30	3.16	3.05
48 h	3.25	3.21	3.33	3.15	3.04
72 h	3.27	3.24	3.36	3.15	3.05

Table XIII. Measured Speed Values For the Sulfur-Sensitized Emulsion Over 72 h of Latent-Image Hold. 0.001 s Exposure Time.

	Speed at D-min + 0.50 (log E)						
Hold Time	Vacuum	0% RH Air	20% RH Air	80% RH Air	0% RH N_2	20% RH N_2	80% RH N_2
0.5 h	2.82	2.80	2.73	2.77	2.89	2.72	2.75
1 h	2.81	2.79	2.74	2.78	2.88	2.72	2.74
4 h	2.80	2.81	2.76	2.80	2.90	2.72	2.74
24 h	2.80	2.80	2.79	2.83	2.88	2.73	2.75
48 h	2.80	2.81	2.79	2.80	2.87	2.73	2.77
72 h	2.79	2.80	2.79	2.82	2.86	2.73	2.76

Table XIV. Measured Speed Values For the Sulfur-Sensitized Emulsion Over 72 h of Latent-Image Hold. 1 s Exposure Time.

	Speed at D-min + 0.50 (log E)				
Hold Time	Vacuum	0% RH Air	20% RH Air	0% RH N_2	20% RH N_2
0.5 h	2.64	2.58	2.60	2.57	2.56
1 h	2.64	2.61	2.61	2.57	2.56
4 h	2.64	2.61	2.64	2.56	2.56
24 h	2.64	2.60	2.64	2.56	2.56
48 h	2.61	2.60	2.64	2.55	2.57
72 h	2.62	2.60	2.63	2.53	2.56

Table XV. Measured Speed Values For the Sulfur-Plus-Gold-Sensitized Emulsion Over 72 h of Latent-Image Hold. 0.001 s Exposure Time.

	Speed at D-min + 0.50 (log E)						
Hold Time	Vacuum	0% RH Air	20% RH Air	80% RH Air	0% RH N_2	20% RH N_2	80% RH N_2
0.5 h	2.66	2.73	2.52	2.53	2.75	2.49	2.49
1 h	2.65	2.66	2.51	2.52	2.74	2.49	2.47
4 h	2.65	2.66	2.51	2.53	2.75	2.49	2.48
24 h	2.64	2.68	2.53	2.53	2.75	2.50	2.49
48 h	2.63	2.65	2.53	2.52	2.73	2.48	2.48
72 h	2.62	2.62	2.52	2.52	2.71	2.49	2.47

Table XVI. Measured Speed Values For the Sulfur-Plus-Gold-Sensitized Emulsion Over 72 h of Latent-Image Hold. 1 s Exposure Time.

	Speed at D-min + 0.50 (log E)				
Hold Time	Vacuum	0% RH Air	20% RH Air	0% RH N_2	20% RH N_2
0.5 h	2.59	2.42	2.43	2.43	2.40
1 h	2.57	2.43	2.43	2.43	2.39
4 h	2.58	2.42	2.45	2.42	2.39
24 h	2.57	2.43	2.44	2.42	2.39
48 h	2.55	2.40	2.44	2.40	2.40
72 h	2.55	2.42	2.43	2.40	2.38

Table XVII. Measured Speeds Obtained During Extended Development for the Unsensitized Emulsion Over 72 h of Latent-Image Hold. 0.001 s Exposure Time.

	D-min (Measured)			Speed at D-min + 0.50 (log E)		
Hold Time	6 Minutes	24 Minutes	48 Minutes	6 Minutes	24 Minutes	48 Minutes
0.5 h	0.04	0.06	0.17	3.31	3.26	3.36
1 h	0.04	0.06	0.17	3.36	3.28	3.34
4 h	0.04	0.06	0.16	3.40	3.30	3.39
24 h	0.04	0.06	0.17	3.44	3.36	3.42
48 h	0.04	0.06	0.16	3.49	3.37	3.47
72 h	0.04	0.06	0.17	3.51	3.42	3.49

Table XVII. Measured Speeds Obtained During Gold Latensification for the Unsensitized Emulsion Over 72 h of Latent-Image Hold. 0.001 s Exposure Time.

	Speed at D-min + 0.50 (log E)		
Hold Time	Gold Latensification	Bromide Bath	20% RH Air
0.5 h	3.29	3.42	3.37
1 h	3.29	3.44	3.38
4 h	3.31	3.46	3.40
24 h	3.34	3.53	3.48
48 h	3.37	3.57	3.51
72 h	3.37	3.60	3.55